

Advances in Direct Oxidation Methanol Fuel Cells

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ABSTRACT

Fuel cells that can operate directly on fuels such as methanol are attractive for low to medium power applications in view of their low weight and volume relative to other power sources. A liquid feed direct methanol fuel cell has been developed based on a proton exchange membrane electrolyte and Pt/Ru and Pt catalyzed fuel and air/O₂ electrodes respectively. The cell has been shown to deliver significant power outputs at temperatures of 60 to 90° C. The cell voltage is near 0.5 V at 300 mA/cm₂ current density and an operating temperature of 90 °C. A deterrent to performance appears to be methanol crossover through the membrane to the oxygen electrode. Further improvements in performance appear possible by minimizing the methanol crossover rate.

INTRODUCTION

Direct oxidation methanol fuel cells (DMFC) are attractive for several defense and transportation applications in view of their lower weight and volume compared to indirect fuel cells (1,2). The weight and volume advantages of direct oxidation fuel cells are due to the fact that they do not require any fuel processing equipment. Elimination of the fuel processor also results in simpler design and operation, higher reliability, less maintenance, and lower capital and operating costs. Further, direct oxidation fuel cells are projected to have rapid and multiple start up capabilities, and the ability to easily follow varying loads.

Under a task sponsored by the Defense Research Projects Agency (DARPA), JPL, USC, and Giner are engaged in the development of direct methanol fuel cells for future defence applications. A near term objective of the program is to identify advanced catalysts and electrolytes and demonstrate the DMFC technology at the cell level. This paper describes the progress made to date on this effort.

Assessment of Catalysts for the Oxidation of Methanol

Anodic oxidation behavior of methanol was investigated in half cells using both supported and unsupported catalysts at a loading of 0.5 mg/cm^2 . In these experiments 0.5 M sulfuric acid was used as the electrolyte along with 0.001 M perfluorooctanesulfonic acid and the fuel concentration was 1.0 M . These half cell experiments were carried out at 45°C . Anodic oxidation characteristics of CH_3OH at various unsupported (Pt-Sn, and Pt-Ru) and supported catalysts (Ii, Pt-Sn, and Pt-Ru) are given Figures 1 & 2. It can be seen from these results that Pt-Ru is most promising among the SOA Pt based catalysts, for the oxidation of methanol. This observation is in agreement with the results reported in the literature (3,4). All further studies were carried out using Pt-Ru catalyst.

Improved kinetics of methanol oxidation on Pt-Ru catalyst was observed with the increase of temperature, catalyst loading, and methanol concentration. Figure 3 reveals a significant reduction of polarization as temperature is raised from 25 to 60°C . Throughout the current density range of 1 to 100 mA/cm^2 the polarization is reduced almost 100 mV by this temperature increase. Figure 4 gives the results of the catalyst loading studies. Results show that an increase in catalyst loading from 1 to 5 mg/cm^2 resulted in the reduction of almost 100 mV polarization throughout the current density range from 1 to 100 mA/cm^2 . Increase of methanol concentration was also found to result in lower anodic polarization for the oxidation of methanol (Figure 5).

Evaluation of Electrolytes for the Oxidation of Methanol

Liquid Electrolytes: Boron trifluoride dihydrate, triflic acid, perfluoroethanesulfonic acid, and perfluorooctanesulfonic acid (C_8 acid) were evaluated as candidate electrolytes for the oxidation of methanol. Experiments were carried out in half cells using activated Pt-Ru gas diffusion electrodes obtained from commercial sources. Pt-Ru electrodes were found to be unstable and dissolve in boron trifluoride electrolyte. Hence no further experiments were carried out with this electrolyte. Anodic oxidation characteristics of methanol in the other three electrolytes are given in Figure 6. Some of the important findings of this study are: a) anodic oxidation of methanol in triflic acid is comparable to its oxidation in sulfuric acid, b) perfluoroethanesulfonic acid was found to be unattractive for the oxidation of methanol, and c) marginally improved oxidation behavior was observed with perfluorooctanesulfonic acid electrolyte.

Solid Polymer Electrolytes: Nafion, a polymer electrolyte membrane (PEM), is an attractive alternate to the liquid electrolytes for liquid feed methanol cells for several reasons including: a) simplifies design, b) simplifies assembly and operation, b) less corrosive, and c) can minimize or eliminate shunt currents. The material has been used quite successfully in gas feed hydrogen/oxygen fuel cells.

For these reasons, Nafion was evaluated as an electrolyte in a liquid feed half cells. A methanol-water mixture only (without acid) was introduced to the fuel compartment. The particular type of membrane was Du Pont Nafion, Type 117. Anode catalyst in this case was a supported Pt-Ru type that was bonded directly to the Nafion. Figure 7 compares performance of this cell with the Nafion electrolyte as well as the previously employed H_2SO_4 electrolyte. From the results it can be seen that methanol oxidation is more facile with Nafion compared to sulfuric acid electrolyte. Hence Nafion was selected as candidate electrolyte in all further studies.

Cell Design:

Design Options: Two cell design options were considered for direct oxidation methanol fuel cells including: a) gas or vapor feed design and b) liquid feed design. Initial considerations indicated that gas feed design is preferable in that it could employ existing fuel cell type gas diffusion electrodes. Furthermore, the gas feed design could operate at higher temperatures that were anticipated to be necessary for high performance. Subsequent deliberations considered the fact that the liquid feed design would not require a vaporizer and would therefore be much simpler in design and operation. The other potential advantages of liquid-feed design are: a) elimination of complex water and thermal management systems, b) multiple use capability of the methanol-water as the fuel, for humidification purposes, and as an efficient stack coolant, and c) significantly lower system size and weight. This cell design does not suffer from the disadvantages of prior liquid-feed cell designs which employed liquid electrolytes. The use of PFM eliminates the problem of troublesome shunt currents and also eliminates problems associated with corrosion of cell components. Tests have shown that the PFM does not degrade with operation and is suitable for continuous operation. Fuel catalysts were found to exhibit improved performance with the solid electrolyte membrane. Therefore it was resolved to pursue the development of a liquid feed design. On this basis JPI began development of liquid feed type direct methanol fuel cells.

Schematic Diagram of Liquid Feed direct methanol fuel cells:

Figure 8 gives a schematic diagram of the complete laboratory type liquid feed methanol system employing the membrane electrolyte. The MEA consists of a layer of Nafion electrolyte, 7 mil thick, with fuel and air/ O_2 electrodes bonded to either side. Electrode dimensions are 2 inch by 2 inch by approximately 10 mil thick. The MEA is positioned between the machined portion of two graphite blocks. The machined area on each block is a rectangular pattern with open channels (designated as flow field) to allow flow of liquid or gas across the electrode surface. Inlet and outlet ports communicate with the flow fields via holes drilled into the carbon blocks and equipped with threaded fittings at the sides of the blocks. Stainless steel support plates, with the same overall

length and width as the carbon plates, are located on the back surface of the plates. The stainless steel plates as well as the carbon blocks are drilled in their outer perimeter to accommodate bolts that are used to compress the assembly for sealing and to provide electrical contact between the electrode and un-recessed area of the flow field.

The methanol solution is introduced into the fuel compartment of the cell via a pump and then returned to a fuel storage reservoir as shown in Figure 8. The end product, carbon dioxide, is entrapped in the exit fuel line and released in the storage reservoir. Pressurized air or O_2 is introduced to the air compartment of the cell and vented without recirculation. Heaters are located on the outside surface of the cell to control cell temperature. Finally, the cell is equipped with a small closed end hole to accommodate an internal thermocouple.

Performance of Liquid feed Direct Methanol fuel Cells

Effect of Temperature: Voltage-current characteristics of the liquid feed direct methanol fuel cell were measured over a range of temperatures with 2 M methanol as fuel and pure O_2 as oxidant. Results are given in Figure 9 in terms of operating cell potential, versus current density. Each point represents an essentially steady state voltage that was achieved after about 5 min of continuous operation at the indicated current density. Inspection of Figure 9 reveals a marked increase in performance with increase in temperature over the range of 30°C to 95 °C. For example, at a potential of 0.55 V, the current density outputs are 10, 45, and 140 mA/cm² at temperatures of 30, 60 and 95 °C, respectively. Similarly, at a potential of 0.50 V, the current density outputs are 20, 110, and 260 mA/cm² at 30, 60 and 95 °C. The trend of increased output with increase in temperature is in accord with that exhibited by other fuel cells. The increased output at higher temperatures is attributed to a combination of factors consisting of a reduction of cell ohmic resistance, activation polarization, and concentration polarization.

Effect of Methanol Concentration: The effect of methanol concentration on the cell performance was also determined. Three separate runs were carried out at 60 °C each with a different fuel concentration of 0.5M, 2.0M, and 4.0 M methanol. The effect of fuel concentration on overall cell performance is given in Figure 10 in terms of voltage-current characteristics. Inspection of these results shows that at high operating current densities, higher cell voltage is obtained with 2M methanol while somewhat lower outputs are obtained with both higher concentrations, 4M methanol, as well as lower concentrations, 0.5M methanol. At lower current densities 0.5 M methanol was found to provide higher cell operating voltage than 2.0 M methanol. On this basis there appears to be an optimum concentration for operation for different current densities. The optimum may be between 0.5M and 2M methanol. The lower performance of the cell at fuel concentrations less than 0.5 M is probably due to the concentration polarization effects. The

poor performance of the cell at higher methanol concentrations was found to be due to the fuel crossover phenomena. Support for the proposed impact of crossover at high concentrations was shown in half cell studies on the oxygen electrode. Therein it was found that the O_2 electrode performance is significantly lowered at higher methanol concentrations (5). For example, the O_2 electrode potential was noted to drop more than 100 mV at 100 mA/cm² as methanol concentration was increased from 2 to 4 M methanol. This finding emphasizes the need to minimize the crossover rate to improve performance of the O_2 electrode, and hence the overall cell performance.

Fuel Utilization Studies: In order to examine fuel utilization, a cell was set up and run continuously at constant current with a finite amount, 200 ml of 1.0 M methanol solution in the circulation tank, and without replenishment of the methanol. Initially, current was set at 1.875 A (75 mA/cm²) and cell temperature was held at 80°C. Results are given in Figure 11, in terms of cell voltage versus percent utilization of the fuel. The utilization was taken as output amp-hrs/theoretical amp-hrs (from the amount of methanol and its electrochemical equivalent). Inspection of this figure reveals that voltage drops sharply at 75 mA/cm² when utilization approaches 60%. The sharp drop in voltage at this point is believed to be associated with concentration polarization of the fuel electrode that is, in turn, due to an inadequate supply of methanol to the electrode. The methanol supply is, in turn, limited by the low methanol concentration at this point (near 0.5 M or less). The phenomena is consistent with prior half cell studies that revealed the onset of high polarization when methanol concentration declines below this level.

Problems and Issues

Performance of the liquid feed methanol fuel cells is already attractive for some applications and is approaching the levels required for electric vehicle propulsion. With some improvements in electrical performance, efficiency, and cost this system can indeed be considered a serious candidate for electric vehicle applications. These improvements can be achieved by developing high performance anode catalysts, new membranes with reduced methanol permeability, methanol insensitive cathode catalysts, and low cost materials (non Pt based catalysts, membranes, biplate materials etc.).

CONCLUSIONS

Some of the major findings of the study are:

1) Pt/Ru catalyzed electrodes are well suited for oxidation of methanol.

2) Performance of Pt/Ru catalyzed carbon electrodes increases with increased temperatures (25 to 60 °C), increased fuel

concentrate on (0.5 to 2 m methanol) , and increased catalyst loading (.5 to 5 mg/cm²).

3) A new liquid feed DMFC has been developed based on a proton exchange membrane electrolyte , Pt/Ru catalyzed fuel electrode, and Pt catalyzed air/O₂ electrodes.

4) The new cell can deliver significant outputs in excess of 250 mA/cm² at potentials near 0.5 V at moderate temperatures less than 190 °F.

ACKNOWLEDGEMENT

The work described here was carried out at the Jet Propulsion Laboratory, California Institute of Technology, in a program sponsored by ARPA under contract with the National Aeronautics and Space Administration.

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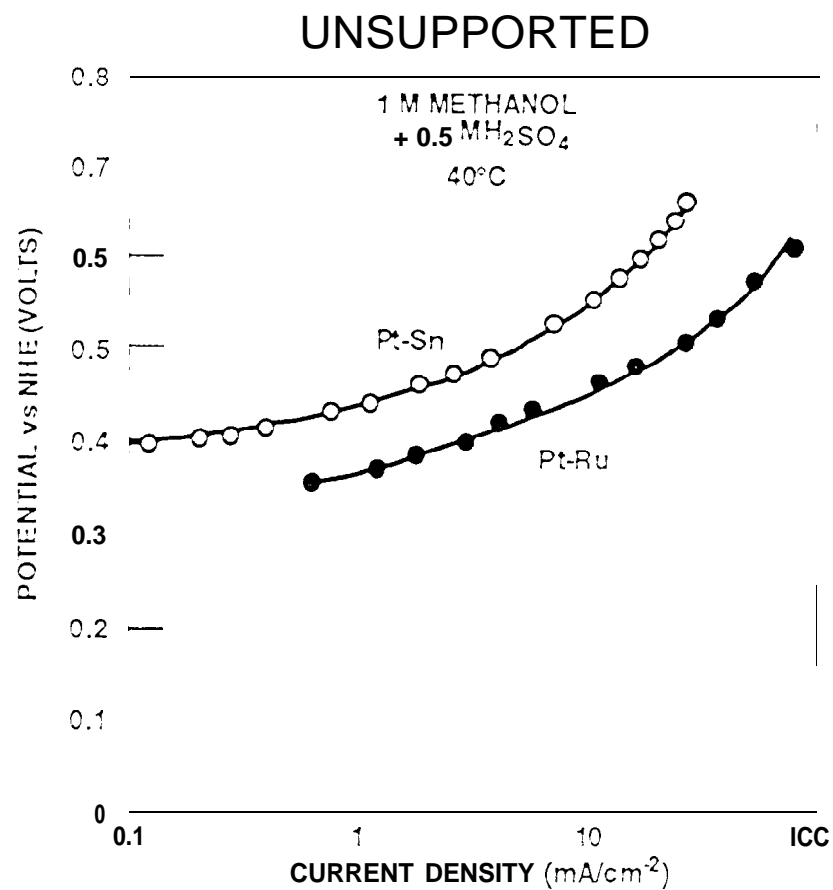


FIGURE 1. EVALUATION OF UNSUPPORTED CATALYSTS FOR METHANOL OXIDATION

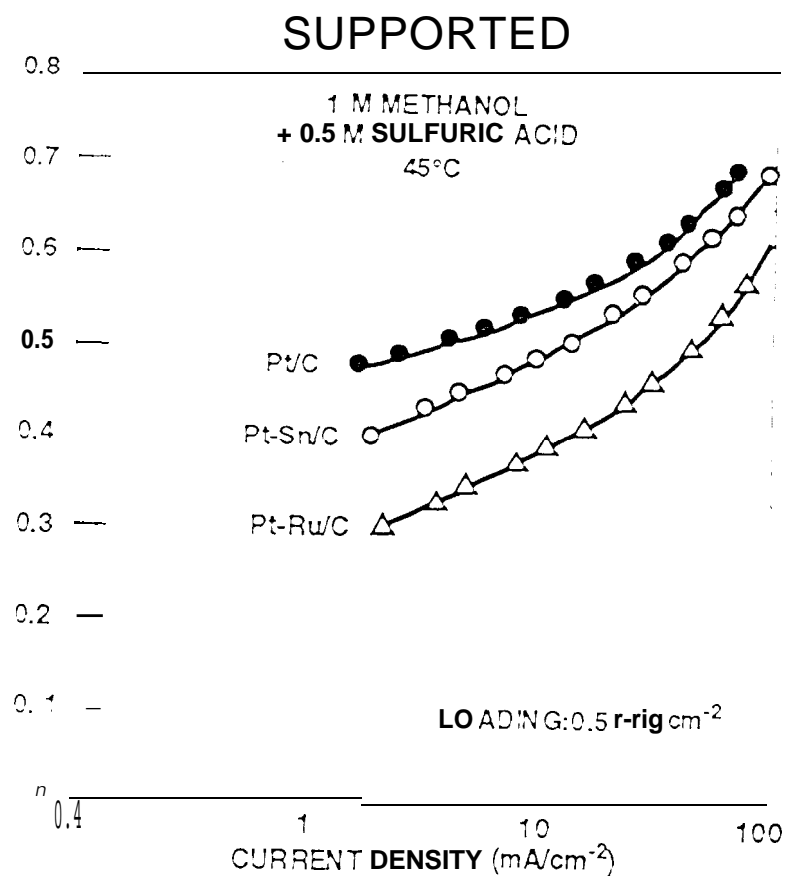


FIGURE 2. EVALUATION OF SUPPORTED CATALYSTS FOR METHANOL OXIDATION

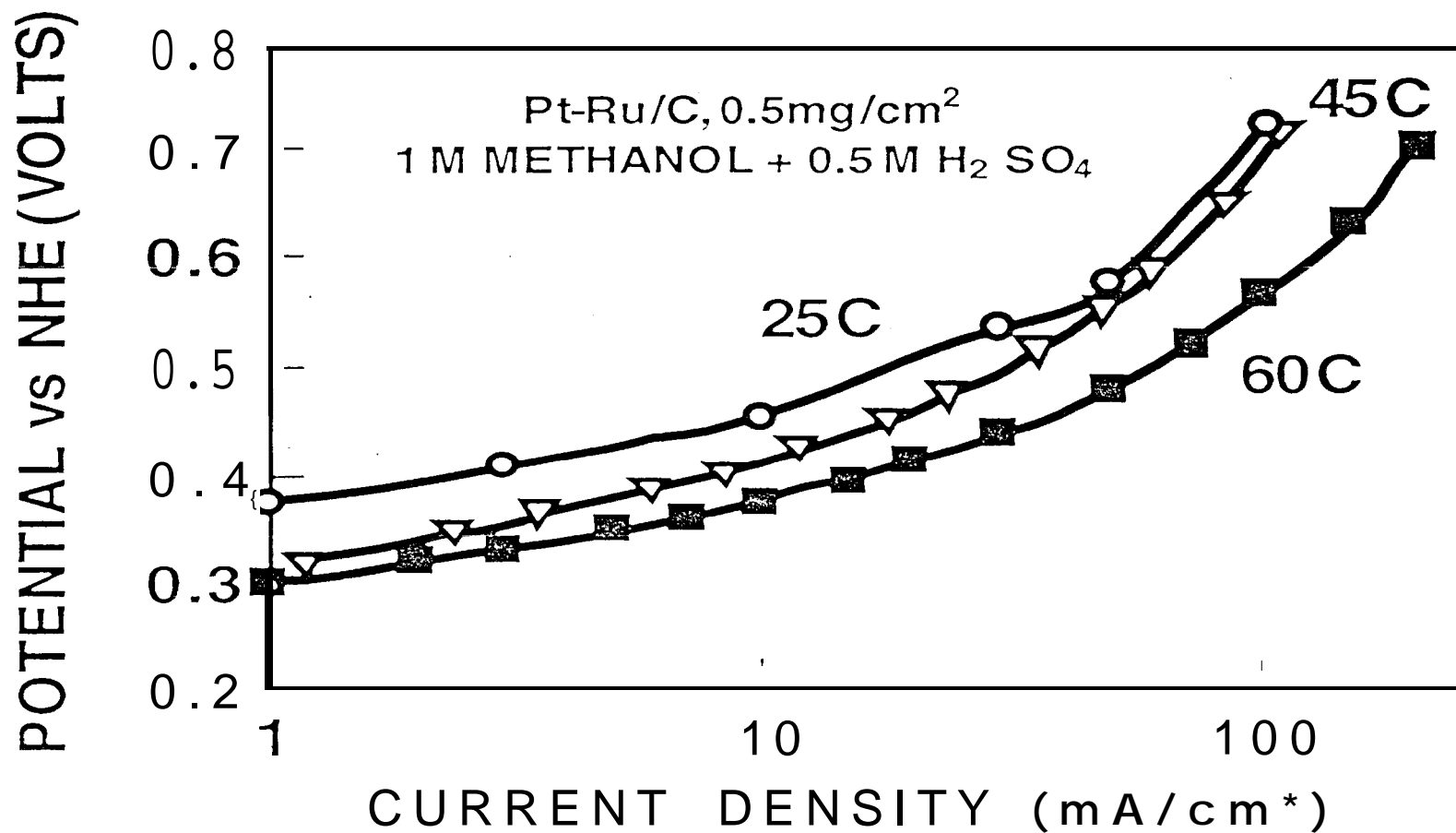


FIGURE 3. EFFECT OF TEMPERATURE ON PERFORMANCE OF PT/RU ELECTRODES

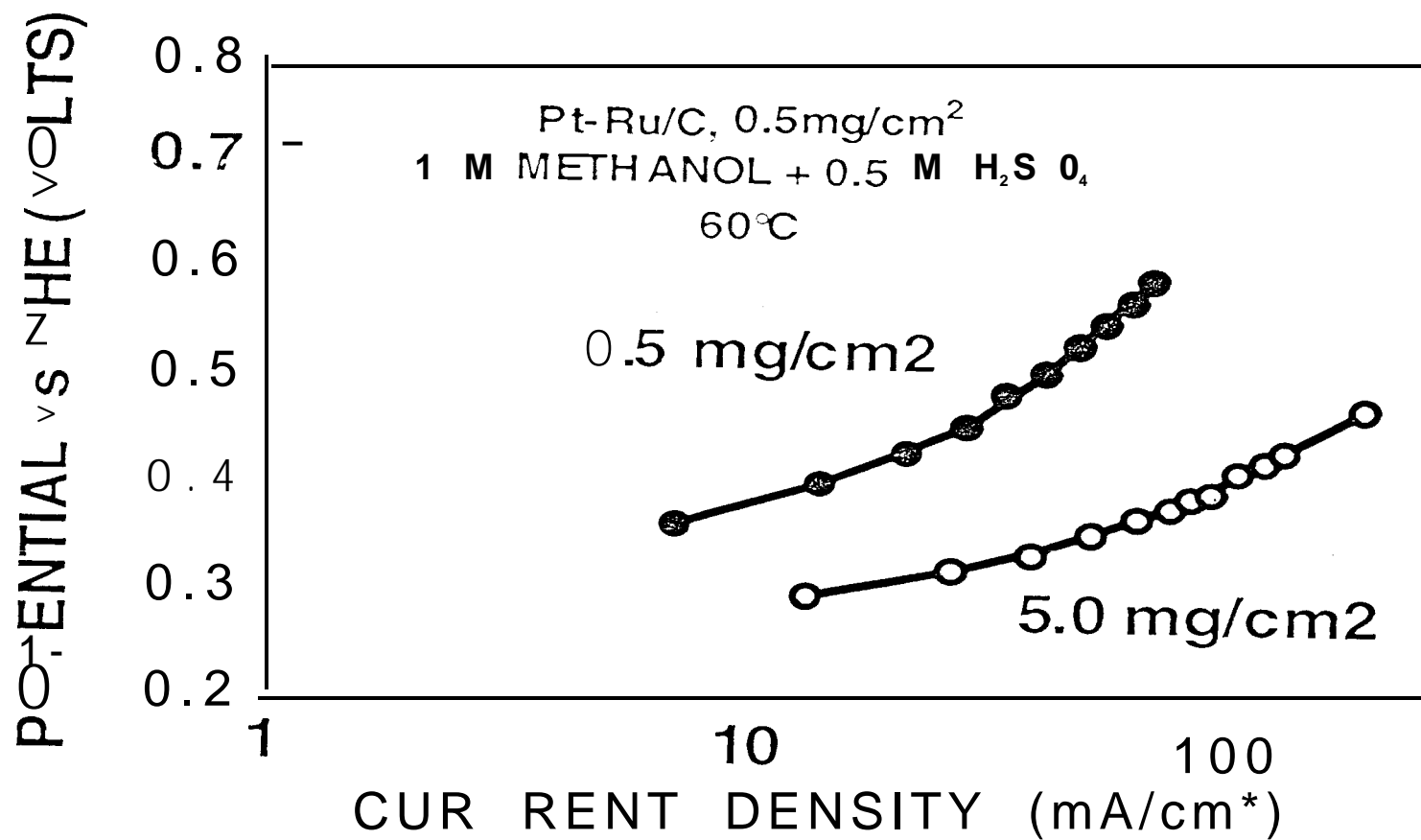


FIGURE 4. EFFECT OF CATALYST LOADING ON PERFORMANCE OF PT/RU ELECTRODES

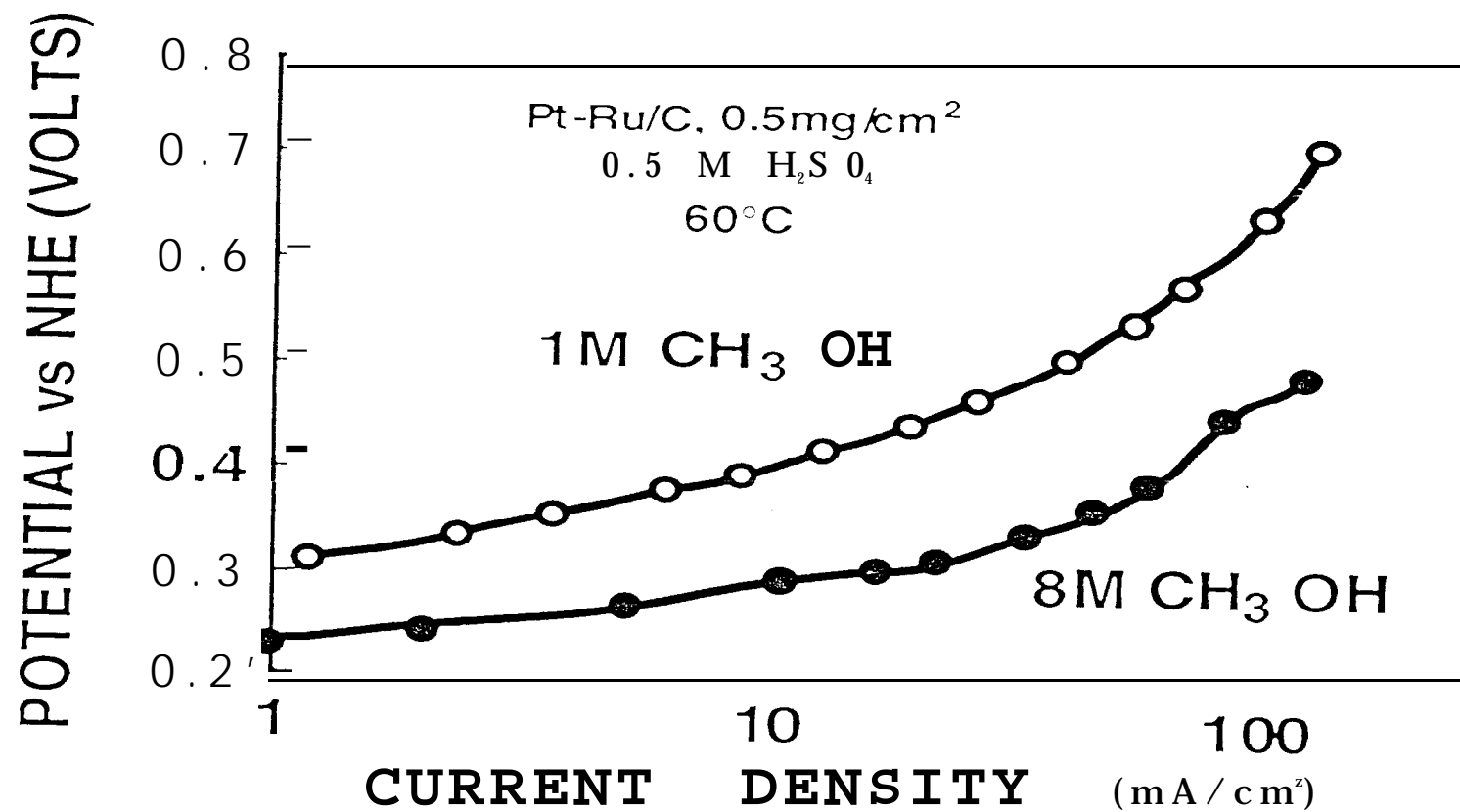


FIGURE 5. EFFECT OF FUEL CONCENTRATION ON PERFORMANCE OF PT/RU ELECTRODES

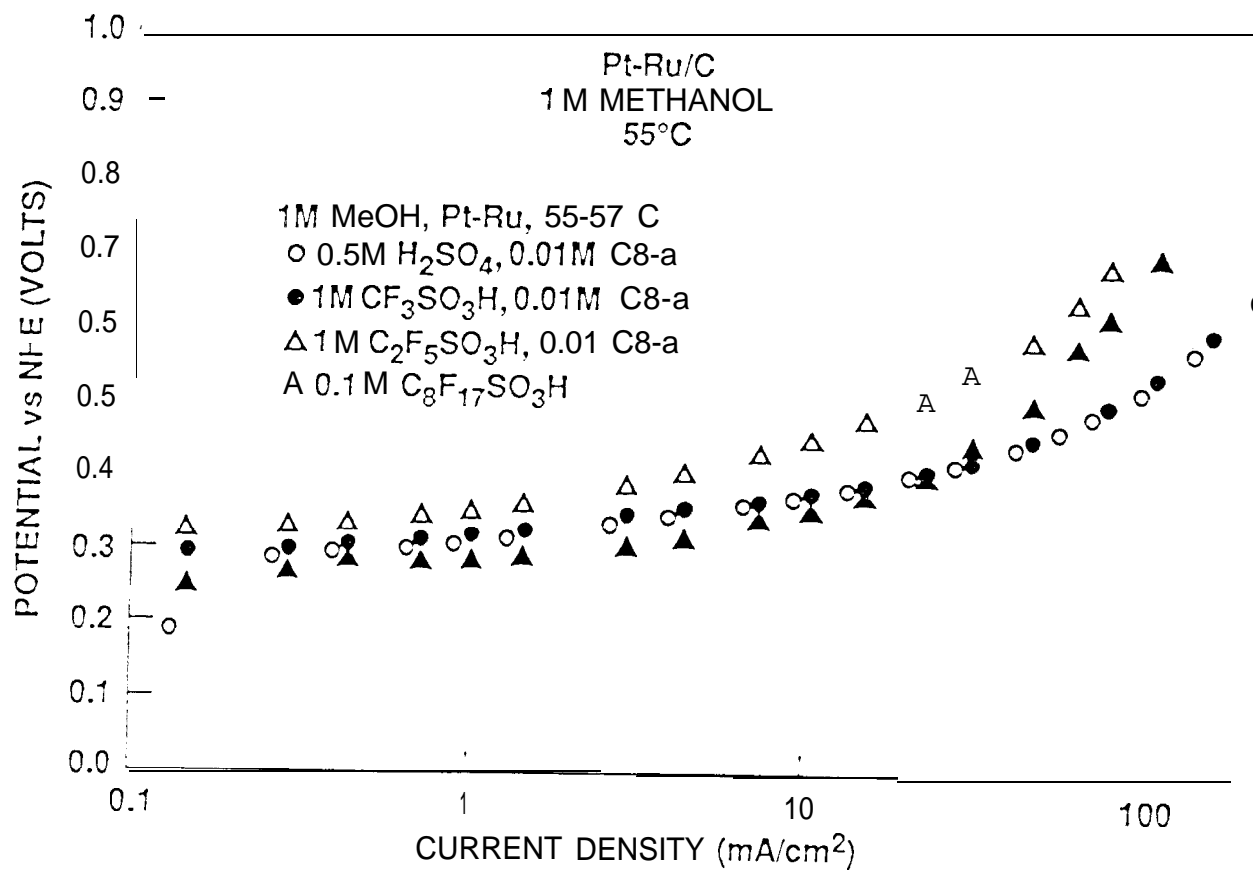
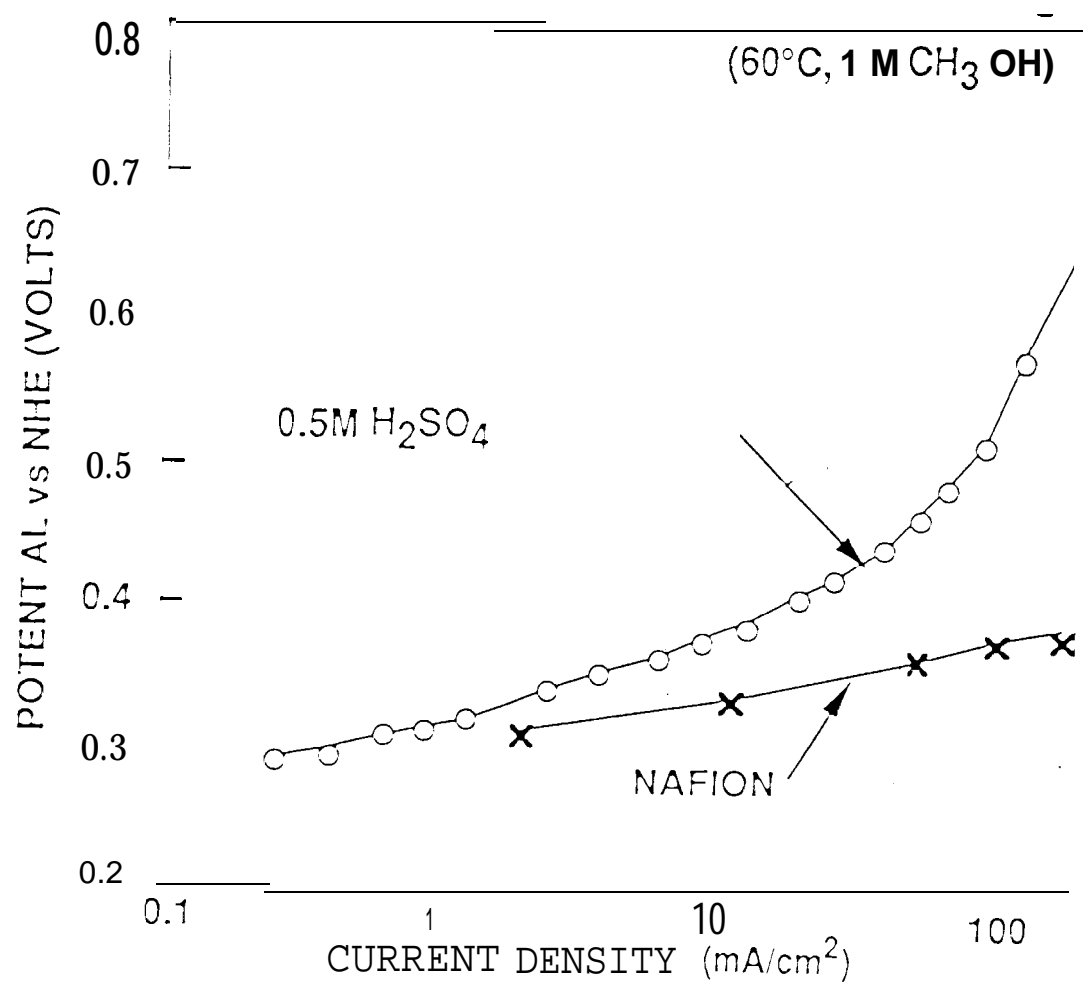


FIGURE 6. ANODIC OXIDATION OF METHANOL
IN VARIOUS ELECTROLYTES



● IMPROVE FUEL OXIDATION CHARACTERISTICS WITH NAFION

FIGURE 7. EVALUATION OF ELECTROLYTES FOR ANODIC OXIDATION OF CH₃OH

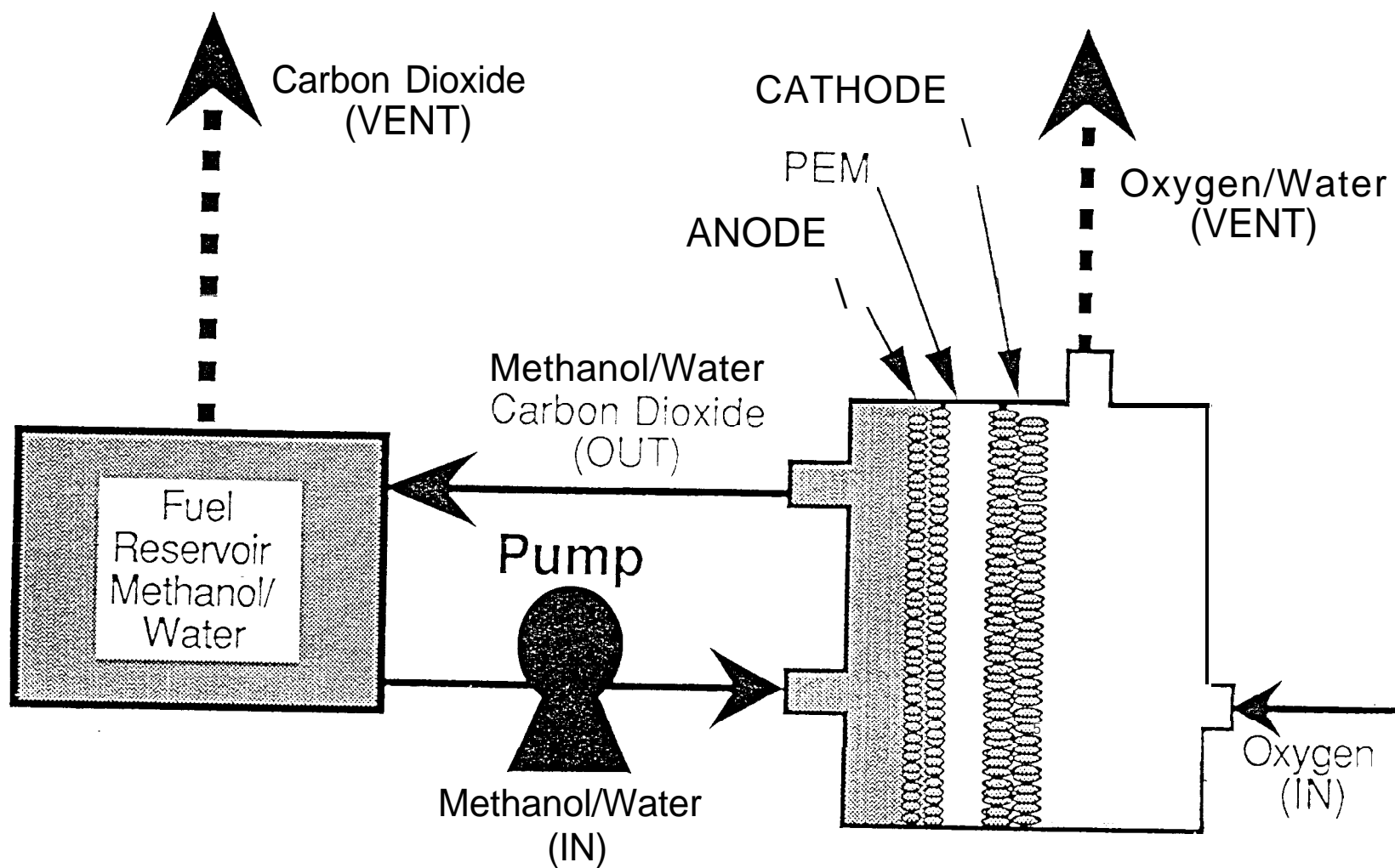


FIGURE 8. DIAGRAM OF JPL LIQUID FEED DIRECT METHANOL FUEL CELL

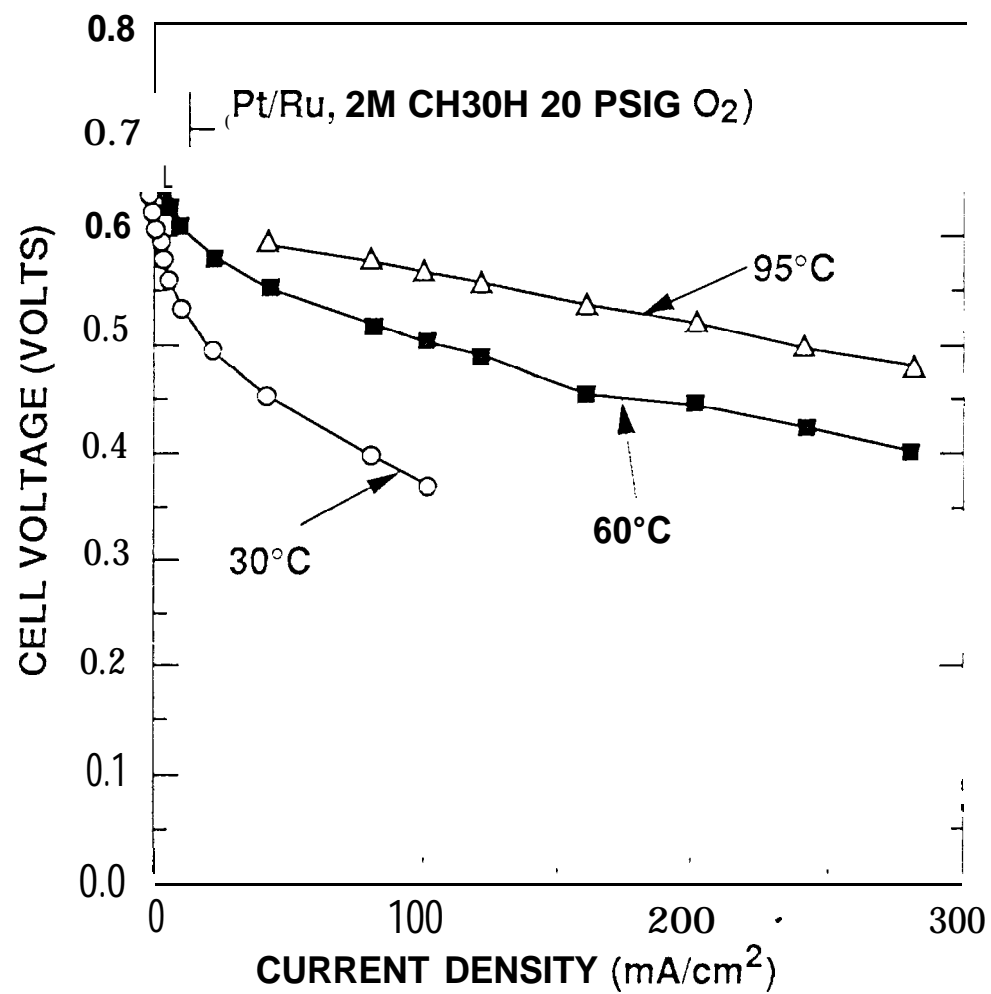


FIGURE 9. EFFECT OF CELL TEMPERATURE ON CELL PERFORMANCE

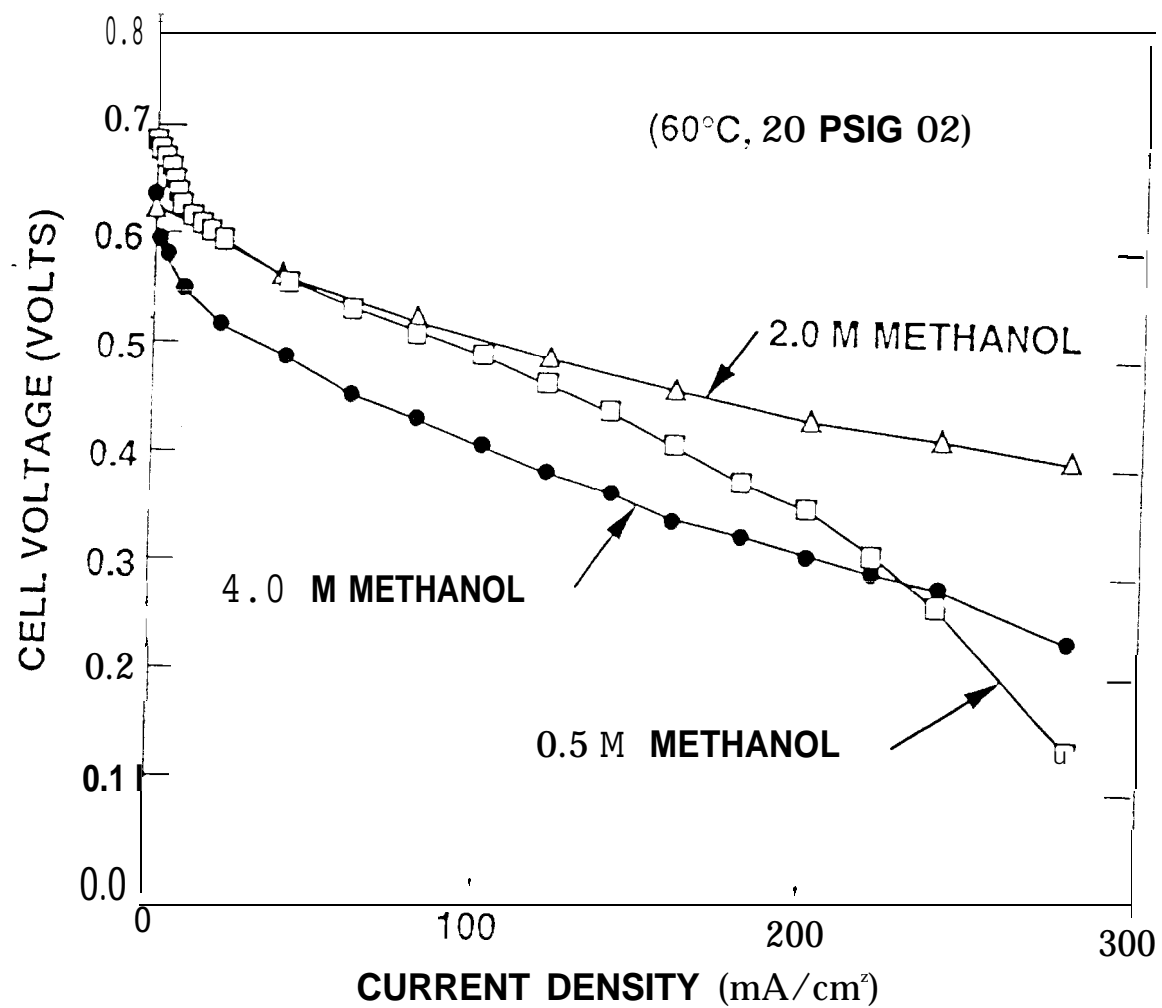


FIGURE 10. EFFECT OF FUEL CONCENTRATION ON CELL PERFORMANCE

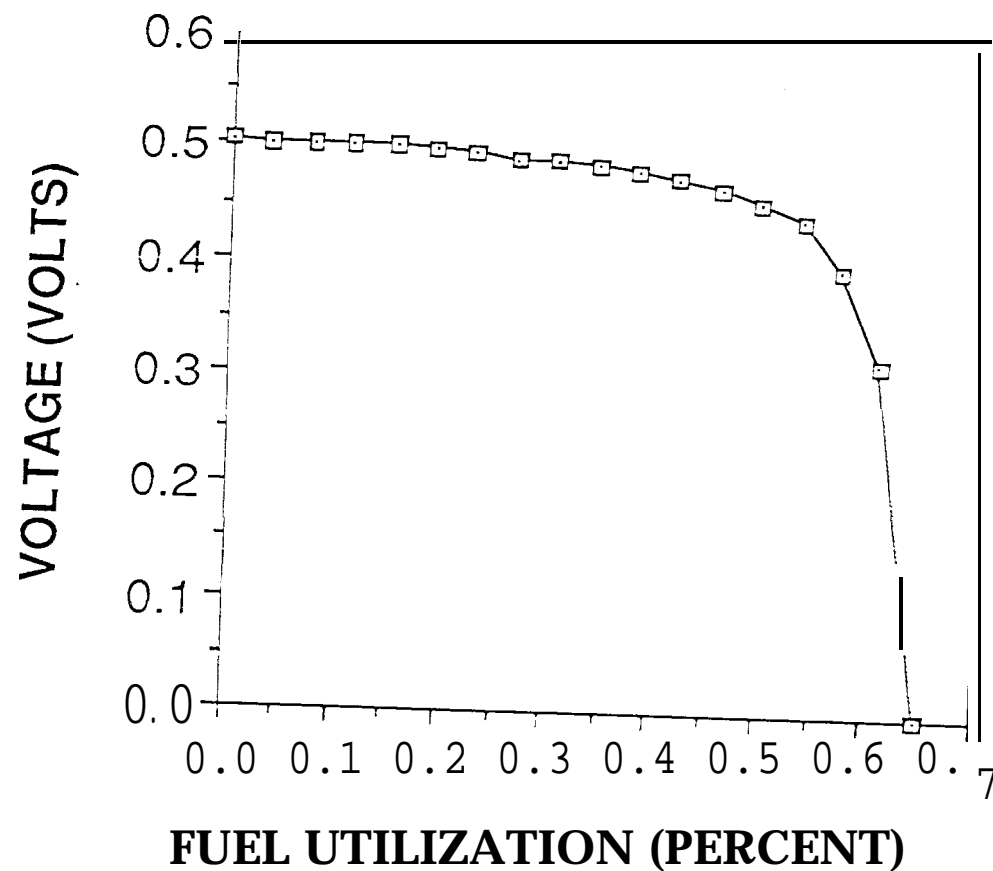


FIGURE 11. VOLTAGE VS. FUEL UTILIZATION CURVE
1 MOLAR METHANOL INITIAL CONCENTRATION
75 mA/cm² CURRENT DENSITY, 62° C, 20 PSIG OXYGEN